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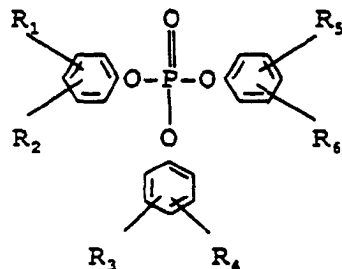
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(54) **Flame retardant compounds, process for their production and flame-retarded organic polymer materials**

(57) Flame retardant compounds obtained by reacting bisphenol A, diphenyl carbonate and a phosphoric acid ester represented by the following general formula (1):



where R<sub>1</sub>-R<sub>6</sub> may be the same or different and each independently represents hydrogen or methyl, a process for their production, and flame-retarded organic polymer materials containing them are provided.

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## Description

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

[0001] The present invention relates to flame retardant compounds, a process for their production and flame-retarded organic polymer materials. The invention particularly relates to flame retardant polymer compounds containing no halogens, to a process for their production, and to organic polymer materials that have been rendered flame retardant thereby.

## 2. Description of the Related Art

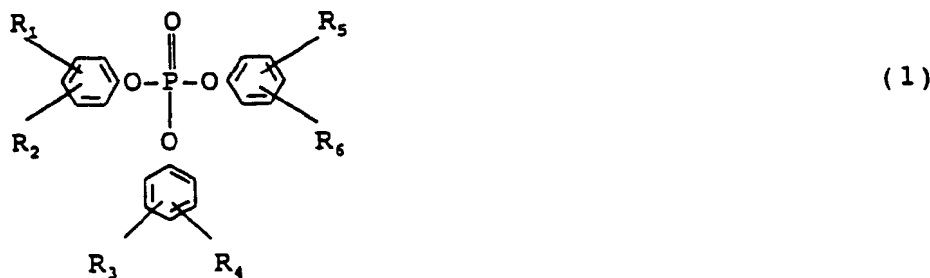
[0002] Organic polymer materials, and especially synthetic resins, are widely used in a variety of fields that take advantage of their diverse properties, and such products require flame retardance as a measure for protection against fire. Known methods used to render organic polymer materials flame retardant include addition of flame retardants comprising halogen-based, phosphorus-based and inorganic compounds.

[0003] However, inorganic compounds are inadequate in terms of their flame-retarding effect, and although halogen-based compounds exhibit an excellent flame-retarding effect it is desirable to minimize their use for safety considerations, while the use of polycarbonate resins and the like has become restricted due to increasing concerns about environmental problems. On the other hand, phosphoric acid esters are the main phosphorus-based compounds used, but they have a problem of volatility due to their low molecular weight.

## BRIEF SUMMARY OF THE INVENTION

[0004] It is therefore an object of the present invention to provide novel flame retardant compounds that exhibit an excellent flame-retarding effect for organic polymer materials while having relatively few environmental pollution problems, as well as a process for their production, and organic polymer materials rendered flame retardant thereby.

[0005] In order to solve the aforementioned problems, the present invention provides a process for production of flame retardant compounds that comprises reacting bisphenol A, diphenyl carbonate and a phosphoric acid ester represented by the following general formula (1):



where  $R_1$ - $R_6$  may be the same or different and each independently represents hydrogen or methyl, and flame retardant compounds obtained thereby.

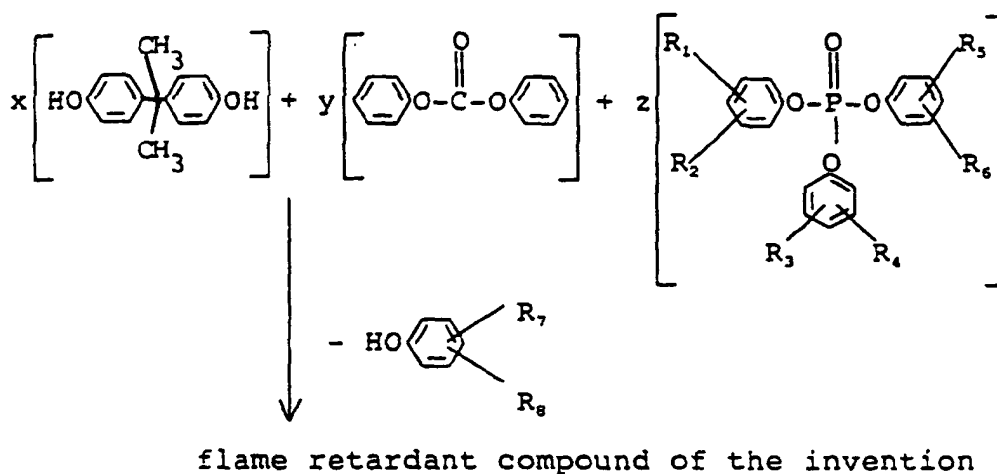
[0006] The invention further provides flame-retarded organic polymer materials containing these flame retardant compounds.

## DETAILED DESCRIPTION OF THE INVENTION

[0007] It is well known that reacting bisphenol A with diphenyl carbonate yields a polycarbonate by an ester exchange reaction, but the present inventors have found that reacting bisphenol A, diphenyl carbonate and a phosphoric acid ester represented by general formula (1) above yields novel compounds having phosphoric acid groups in a portion of the polycarbonate structure, and that these compounds exhibit an excellent flame-retarding effect on organic polymer compounds; the present invention has been completed on the basis of this finding.

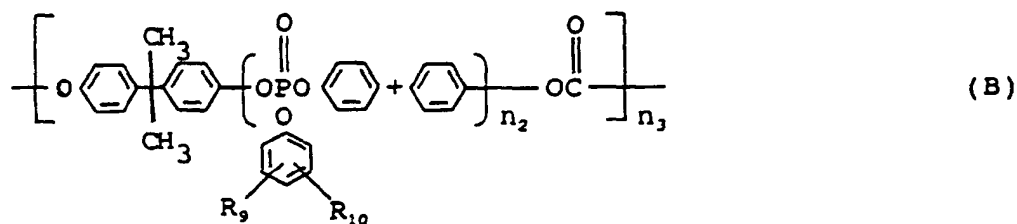
[0008] The reaction of these three different compounds is promoted by mixing the three starting compounds, heating and stirring them in the presence of a common ester exchange reaction catalyst, such as any of various basic com-

pounds, ammonium salts, phosphonium salts and the like, and then distilling out of the system the phenol or methyl-substituted phenol by-products. Here, the charging ratios of the three starting compounds can be varied to obtain polymer compounds with different molecular compositions, according to the following reaction formula.



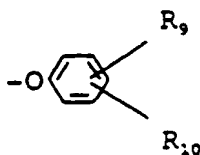
(where x, y and z are any desired positive integers, and R<sub>1</sub>-R<sub>8</sub> may be the same or different and each independently represents hydrogen or methyl).

[0009] The flame retardant compounds of the invention obtained in this manner are believed to have a molecular structure comprising a structural unit represented by the following formula (A) which is a polycarbonate structural unit, and a structural unit represented by the following formula (B) which is a structural unit having a phosphoric acid group introduced into the structure.



where R<sub>9</sub> and R<sub>10</sub> may be the same or different and each independently represents hydrogen or methyl, n<sub>1</sub> is 0 or a positive integer, and n<sub>2</sub> and n<sub>3</sub> each represent positive integers. The arrangement of the structural units of general formula (A) and the structural units of general formula (B) need not be regular.

[0010] In the flame retardant compounds of the invention, the phenoxy group



present in the structural unit of general formula (B) can further undergo ester exchange reaction, so that a portion thereof can have a three-dimensional crosslinked structure.

[0011] A flame retardant compound according to the invention preferably has a weight average molecular weight of 2000-30,000.

[0012] The flame retardant compounds of the invention are themselves flame-resistant polymer compounds, but they are also useful as flame retardants to be added to various organic polymer materials as polycarbonates, polyolefins, polyesters, styrene-based polymers, acrylic polymers and the like, and they produce virtually no environmental pollution or volatile products.

[0013] The present invention will now be explained more fully by way of examples.

#### Example 1

[0014] A branched distillation tube comprising a thermometer, a stirrer, a condenser and a receptacle was mounted on a 200-ml 4-necked flask, and then 45.6 g (0.2 mole) of bisphenol A and 0.1 g ( $3.3 \times 10^{-4}$  mole) of a tetrabutylammonium acetate catalyst were charged therein, and heated. Upon dissolution at 160°C, the mixture was stirred while charging 32.6 g (0.1 mole) of triphenyl phosphate, and the phenol was distilled off under reduced pressure. The reaction was suspended when phenol efflux ceased at an internal temperature of 190°C and reduced pressure of 5 mmHg, and the mixture was then cooled to 150°C. After next adding 23.5 g (0.11 mole) of diphenyl carbonate and again heating to dissolution, the phenol was distilled off under reduced pressure in the same manner as above. The reaction was completed when phenol efflux ceased at an internal temperature of 190°C and reduced pressure of 5 mmHg. A yield of 64 g was obtained.

[0015] Based on HPLC (GPC) analysis, the reaction rate for bisphenol A was 99.3%, the reaction rate for triphenyl phosphate was 94.6%, and the weight average molecular weight of the product was 8600. The phosphorus content of the product was 4.7%, and the melting point was 77-82°C.

#### Examples 2-6

[0016] The procedure of Example 1 was repeated, except that the charging amounts (moles) for bisphenol A (BPA), tetrabutylammonium acetate (TBAA), triphenyl phosphate (TPP) and diphenyl carbonate (DPC) were changed as shown in Table 1, or tricresyl phosphate (TCP) was used instead of TPP. The results are summarized in Table 1.

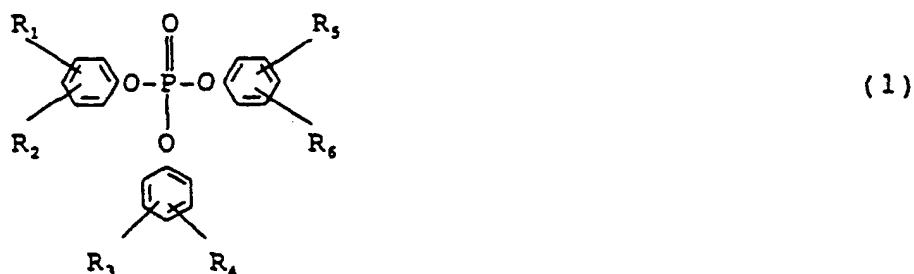
Table 1

Example No.	2	3	4	5	6
BPA (mole)	0.3	0.4	0.2	0.3	0.2
TPP (mole)	0.1	0.1	-	-	-
TCP (mole)	-	-	0.1	0.1	0.17
TBAA (mole)	$3.3 \times 10^{-4}$	$8.0 \times 10^{-4}$	$1.0 \times 10^{-3}$	$1.6 \times 10^{-3}$	$1.0 \times 10^{-3}$
DPC (mole)	0.21	0.31	0.11	0.21	0.037
BPA reaction rate (%)	99.3	100	100	100	95.4
Phosphate reaction rate (%)	89.2	91.1	85.2	79.4	85.3
P content (%)	3.3	2.6	4.3	3.1	6.4
Melting point(°C)	74-81	110-120	104-121	72-96	66-96
Wt. average mol. wt.	4100	12300	8400	5900	3400

[0017] According to the invention there are provided flame retardant compounds with an excellent flame-retarding effect on organic polymer materials and virtually no problems of environmental pollution or volatility. It is thereby possible to obtain organic polymer material products with excellent flame retardant properties.

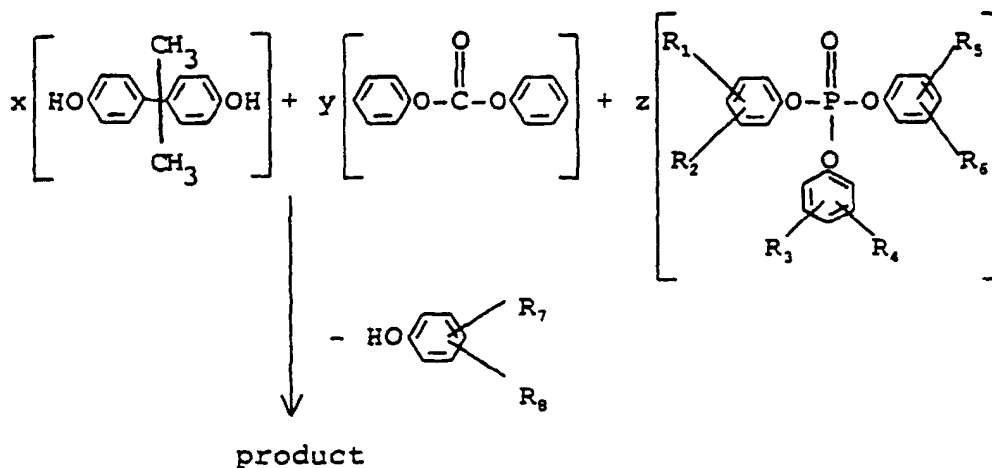
## Claims

1. A flame retardant compound obtained by reacting bisphenol A, diphenyl carbonate and a phosphoric acid ester represented by the following general formula (1):



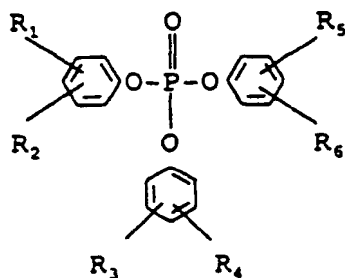
where  $\text{R}_1$ - $\text{R}_6$  may be the same or different and each independently represents hydrogen or methyl.

2. A compound according to claim 1, which is obtained by the reaction according to the following formula.



where  $x$ ,  $y$  and  $z$  are any desired positive integers, and  $\text{R}_1$ - $\text{R}_8$  may be the same or different and each independently represents hydrogen or methyl.

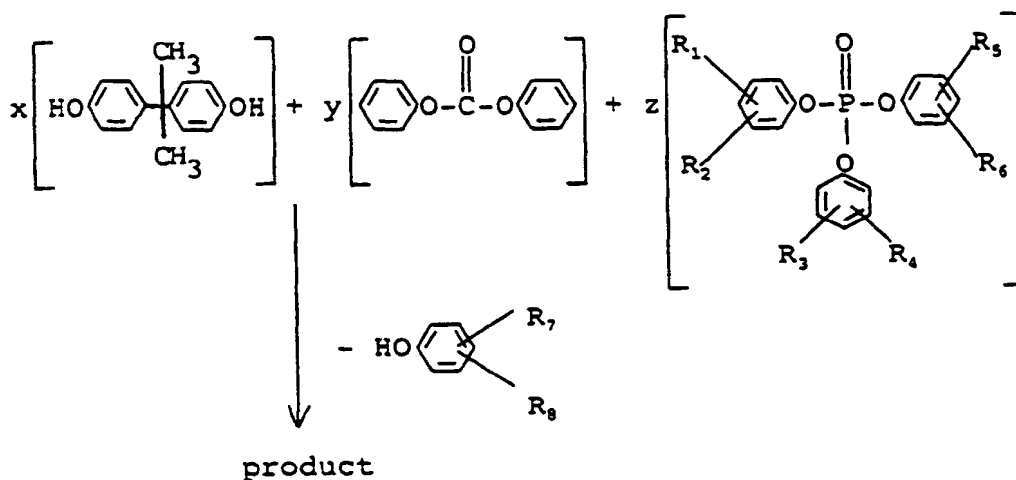
3. A compound according to claim 1, which has a weight average molecular weight of 2000-30,000.
4. A process for production of flame retardant compounds that comprises reacting bisphenol A, diphenyl carbonate and a phosphoric acid ester represented by the following general formula (1):



(1)

where  $\text{R}_1$ - $\text{R}_6$  may be the same or different and each independently represents hydrogen or methyl.

5. A process according to claim 4, wherein the reaction is carried out according to the following formula.



where  $x$ ,  $y$  and  $z$  are any desired positive integers, and  $\text{R}_1$ - $\text{R}_8$  may be the same or different and each independently represents hydrogen or methyl.

6. A flame-retarded organic polymer material that contains a flame retardant compound according to claim 1.
7. A material according to claim 6, wherein the organic polymer material is selected from among polycarbonates, polyolefins, polyesters, styrene-based polymers and acrylic polymers.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 00 30 0779

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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X	* claims 1,5,11 *	1,4,6	
A	GB 1 405 983 A (MITSUBISHI) 10 September 1975 (1975-09-10) * page 15, column 2; table 3 *	1,3,6	
A	EP 0 021 216 A (BAYER AG) 7 January 1981 (1981-01-07) * page 10, line 4 - line 10; claims 1,6 *	1,2,6	
A	EP 0 103 227 A (BAYER AG) 21 March 1984 (1984-03-21) * claims 1,2,4 *	1,3	
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 462 (C-1101), 24 August 1993 (1993-08-24) & JP 05 112636 A (UBE IND LTD), 7 May 1993 (1993-05-07) * abstract *	1,4	<div>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</div> <div>C08G C08L C08K C09K</div>
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>11 May 2000</b>	Examiner <b>Engel, S</b>
<div>CATEGORY OF CITED DOCUMENTS</div> <div> X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document  T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document </div>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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EP 00 30 0779

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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